Review

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Thiol-yne click polymerization

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The research on using thiol-ene click reaction to synthesize sulfur-containing polymers with topological structures and advanced functional properties is a hot topic. However, the application of the thiol-yne reaction in the functional polymer preparation is limited and the thiol-yne click polymerization is to be further developed. In this review, we summarized recent research efforts on using thiol-yne click polymerization to synthesize polymers with topological structures. The sulfur-containing polymers were facilely prepared by photo- and thermo-initiated, amine-mediated, and transition-metal-catalyzed thiol-yne click polymerizations. These polymers are promising to be used as drug-delivery vehicles, high refractive index optical materials, photovoltaic materials, and biomaterials etc.

thiol-yne click polymerization, radical mechanism, amine, rhodium complex, function

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The exploration of new polymerization method for the preparation of functional polymers with unique structures is of vital importance to polymer science. Generally, the polymerization methods were established from the efficient organic reactions [1]. The click chemistry, proposed by Sharpless and co-workers [2] in 2001, enjoys the remarkable advantages of mild reaction conditions, regioselectivity, high reaction rate, functionality tolerance and atom economy etc., and the click reaction is ideally to be developed into a polymerization technique. Indeed, the azide-alkyne click polymerizations were successfully established and functional polytriazoles were prepared [3–6].

During the course of development of azide-alkyne click reactions, the thiol-ene and Diels-Alder (DA) reactions have been identified to possess the "click" features [7–13]. Similar to the thiol-ene click reaction, the thiol-yne one could also be included into the catalogue of click reactions [14,15]. Moreover, the thiol-yne click reaction has the additional feature that two thiol groups could react with one ethynyl group via well-known two-step processes, and fully additive products with branched structures will be yielded [16]. Meanwhile, the mono-additive products of vinyl sulfides could also be obtained when the reactions were carried out between aromatic alkyne and thiols [17,18]. Theoretically, there are regio- and stereo-isomers of the yielded vinyl sulfides, as shown in Figure 1, which could be well-controlled by catalyst selection.

The efficiency of thiol-yne click reaction makes it promising to be developed into a thiol-yne click polymerization

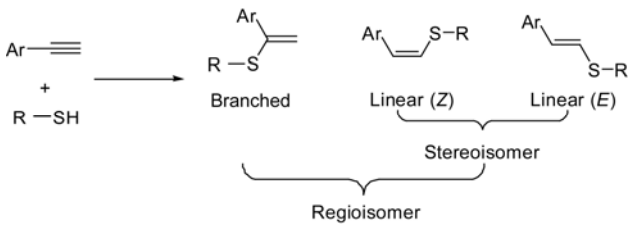

Figure 1 The schematic products of click reactions between aromatic alkynes and thiols.

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technique for the synthesis of functional polymers with novel structures [7]. Indeed, the thiol-yne click reaction has been used to synthesize functional polymers with sulfur-containing linear and topological structures [17–28], which have been widely applied in diverse areas [17,18,29]. While, to our best knowledge, there is no review to summarize its recent progress. In this paper, we reviewed the progress of thiol-yne click polymerization and its application in preparing sulfur-containing polymers with topological structures.

From the viewpoint of mechanism, the thiol-yne click (polymerization) reactions have three types: free-radical, amine-mediated, and transition-metal catalyzed processes. Moreover, depending on the initiator, the free radical process could be further divided into photo- and thermo-initiated reactions.

Figure 2 shows the radical mediated two cycle mechanism of the prevalent thiol-yne click reaction [16]. In the first cycle, the thiyl radicals will be generated from thiol groups by photo- or thermo-initiation process. Then, the thiyl radical adds across the ethynyl group to form a vinyl sulfide radical, which could attract a hydrogen atom from a thiol group, producing the vinyl sulfide and generating another thiyl radical at the same time. In certain conditions, the cycle 2 will subsequently follow: a thiyl radical adds across the double bond of the vinyl sulfide, generating a dithioether radical, which attracts a hydrogen atom from a thiol groups and forms the disubstituted product and a new thiyl radical.

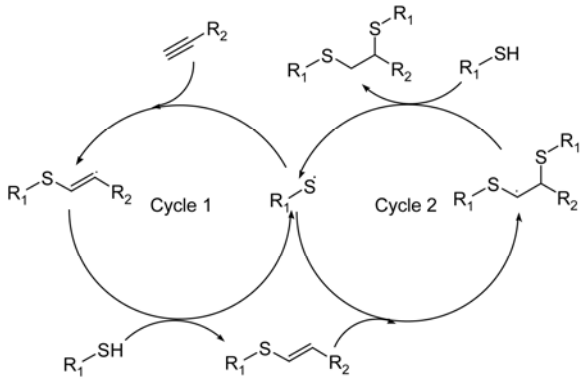

Figure 2 Radical mediated mechanism of the thiol-yne click reaction.

1 Photo-initiated thiol-yne click polymerization

1.1 Preparation of hyperbranched polymers

Unlike the dendrimers, the hyperbranched polymers could be easily prepared via a one-step process in one-pot reaction [30–32]. Featured by the compact branched structure, multiple end-functionalities and 3-dimensional scaffold, hyperbranched polymers have potential utility as drug-delivery vehicles, catalytic supports, viscosity modifiers etc. [33]. As discussed above, the two thiol groups could react with one ethynyl group via two-step addition processes, which makes the thiol-yne click polymerization a popular method for the preparation of hyperbranched polymers. The additional benefit of this technique is its versatility in terms of reaction conditions and the tolerance to most of functional groups.

In 2009, Perrier and coworkers [21] reported the synthesis of functional hyperbranched polymers by photo-initiated thiol-yne click polymerization under the assistance of the initiator of 2,2-dimethoxy-2-phenylacetophenone (DMPA). As shown in Figure 3, sulfur-containing hyperbranched polymers (*hb*-P**I** and *hb*-P**II**) were synthesized from prop-2-ynyl-3-mercaptopropanoate (PYMP) and a macromonomer of ATPST, respectively. It is worth noting that the ^{1}H NMR spectra showed that minimal amounts of ethynyl groups after the polymerization were remaining, indicating that the

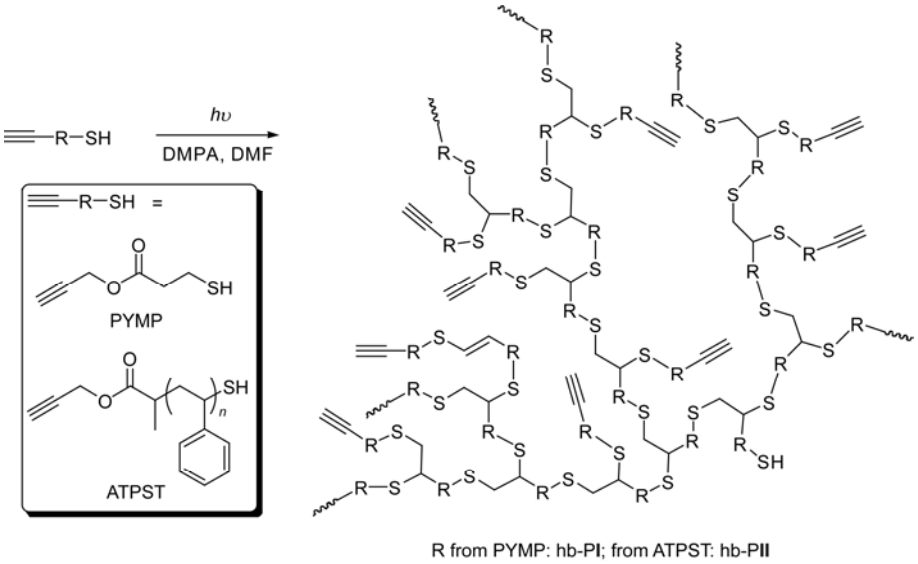

Figure 3 Synthetic routes to hyperbranched polymers by the thiol-yne click polymerizations.

degree of branching (DB) of *hb*-P**I** and *hb*-P**II** could reach unity. This value is much higher than that of the polymers prepared from conventional polymerization methods, which produce hyperbranched polymers with DB values of approximately 0.5.

Thanks to the click feature of this polymerization, a wide variety of functional groups could be incorporated into the hyperbranched polymers by using various macromonomers. An example was also reported by Perrier and coworkers in 2011 (Figure 4) [22]. They first designed and synthesized linear block macromonomers of P**III** and P**IV** from dimethyl acrylamide/*t*-butyl acrylate and styrene monomers by reversible addition-fragmentation chain transfer polymerizations. These macromonomers were then facilely polymerized to produce hyperbranched block copolymers of *hb*-P**V** and *hb*-P**VI**. They also studied their self-assemble behavior, and found that *hb*-P**V** gave rise to large aggregates in water acetone mixtures, while the hydrolyzed products of *hb*-P**VI** intended to form very large aggregates when the acrylic acid group is unionized, but gave well defined small particles when the acid groups were ionized. Hence, these hyperbranched polymers could be potentially used for drug delivery.

The procedure for the preparation of the monomers containing both of thiol and ethynyl groups is, however, quite tedious. Recently, Gao and coworkers reported a new strategy for preparing the monomers and hyperbranched polymers by combination of thiol-halogen click-like reaction and thiol-yne click polymerization (Figure 5) [19]. *hb*-P**VII** and *hb*-P**VIII** with high molecular weights were facilely prepared. This strategy shows the advantages of simplicity, rapidness, flexibility, generality, modular character and high efficiency. Therefore, this work opens a new avenue for facile and scalable preparation of hyperbranched polymers [31].

1.2 Preparation of polymer networks

The photo-initiated step-growth thiol-ene polymerization could produce polymer networks with highly uniform structures and few unreacted functional groups. The cross-linking density of the polymer networks is, however, relatively low unless increasing the monomer functionality. The thiol-yne click polymerization could overcome this shortcoming. Bowman, Lowe and coworkers [24–26] have succeeded in preparing highly cross-linked polymer networks with high glass transition temperature by this technique.

Figure 6 shows some structures of commercially available multifunctional thiols (**4–6**) and multifunctional alkynes (**7–9**), which were used to prepare the polymer networks. The photo-initiated thiol-yne click polymerizations mediated by 1-hydroxy-cyclohexyl phenyl ketone (Irgacure 184) proceeded rapidly and uniform networks with relatively narrow differential scanning calorimetry and dynamic mechanical analysis glass transition ranges were yielded. Due to the sulfide linkages, the polymer networks have refractive index values as high as 1.66, which is proportional to the weight percent of sulfur groups. The results demonstrate that the thiol-yne click polymerization could be employed as a rapid high-throughput technique to prepare networks and to study their structure-property relationships.

1.3 Preparation of linear main chain polymers

According to the reaction nature of thiol-yne click polymerization that two thiol groups could be added to one ethynyl group by two-step processes, the hyperbranched polymers and cross-linked networks could be easily prepared. The use of this polymerization to synthesize linear main chain polymers bearing different side-chain functionalities is, however, a hard task. In 2012, Turunc and Meier [28] reported that linear main chain polymers could be prepared by the UV-initiated click polymerizations of terminal monoynes with dithiols (Figure 7). This strategy is convenient and versatile, making it possible to synthesize comb-shaped polymers by selection of monoyne and dithiol monomers [34].

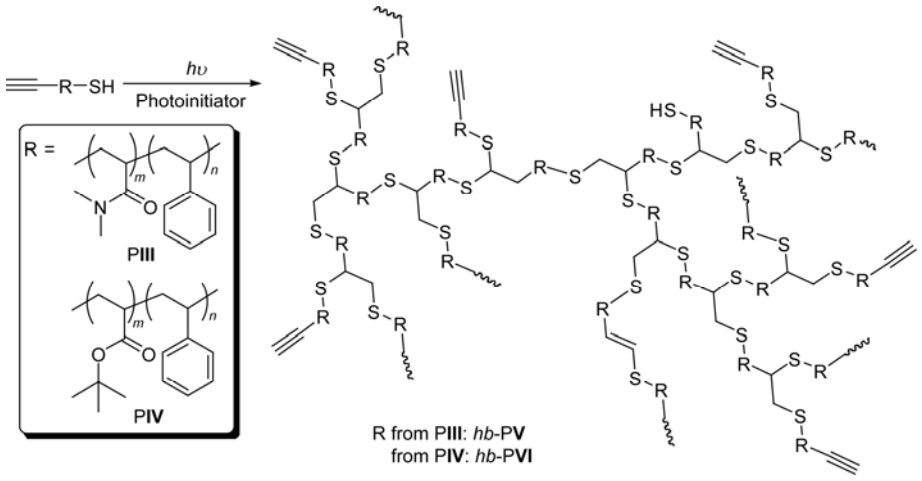

Figure 4 Synthesis of sulfur-containing hyperbranched block copolymers by thiol-yne click polymerizations.

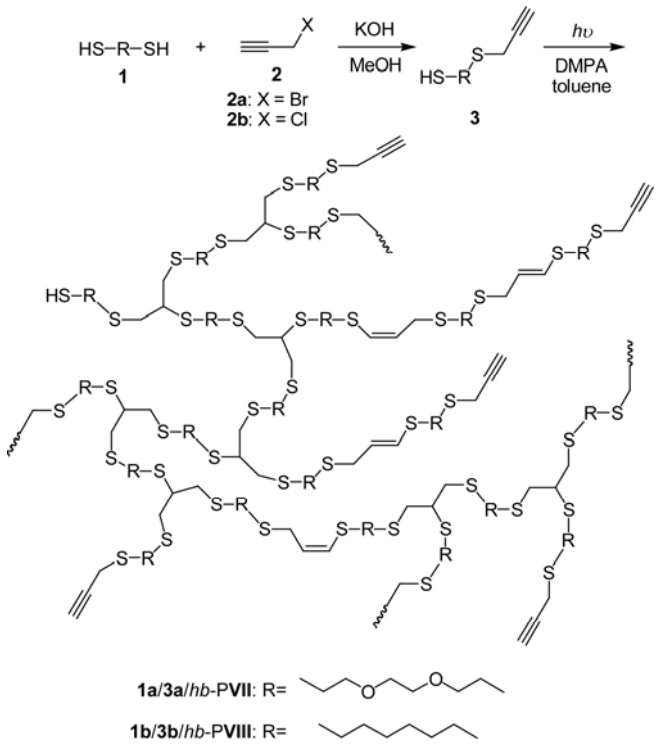

Figure 5 Synthesis of hyperbranched polymers by combination of thiol-halogen click-like reactions and thiol-yne click polymerizations.

2 Thermo-initiated thiol-yne click polymerization

Not only could the UV light initiate thiol-yne click polymerization, the heat could play the same role. The application of thermo-initiated thiol-yne click polymerization in polymer preparation is, however, rare because the efficiency of thermo-initiated polymerization was relatively low compared to photo-initiated one (Figure 8) [28].

Gao and coworkers [20] reported the synthesis of hyperbranched polymers from commercial available intermediates **14** and **15** using sequential thiol-ene addition and thiol-yne click polymerization. The polymerization propagated smoothly in the presence of azobisisbutyronitrile (AIBN), a radical generator, under heating, and hyperbranched polymers *hb*-P**XI** with high molecular weights (M_w) and high DB values were produced (Figure 9). Interestingly, the M_w and DB of polymers could be fine-tuned through polymerization time. *hb*-P**XI** are promising to find high-tech applications due to their internal thiol and ether groups, peripheral alkyne groups, and highly branched architecture.

Our group has been working on the development of new polymerization reactions based on triple-bond building blocks [1]. Attracted by the versatility and efficiency of the thiol-yne click polymerization and as a nature extension of our research, we also embarked on a project in this emerging field. We found that thiol-yne polymerization can be carried out by heating without any additive. As shown in Figure 10, mono-additive products of poly(vinylene sulfide)s (PVSs) P**XII** could be obtained when dithiol **18** was reacted with aromatic diynes **17**, probably due to the conjugation effect of triple bonds with the aromatic benzene ring. More importantly, this polymerization is quite efficient and linear PVSs with M_w up to 60000 could be obtained even the reaction was carried out at 30°C for only 2 h. Furthermore, by incorporating various functional groups into the aromatic

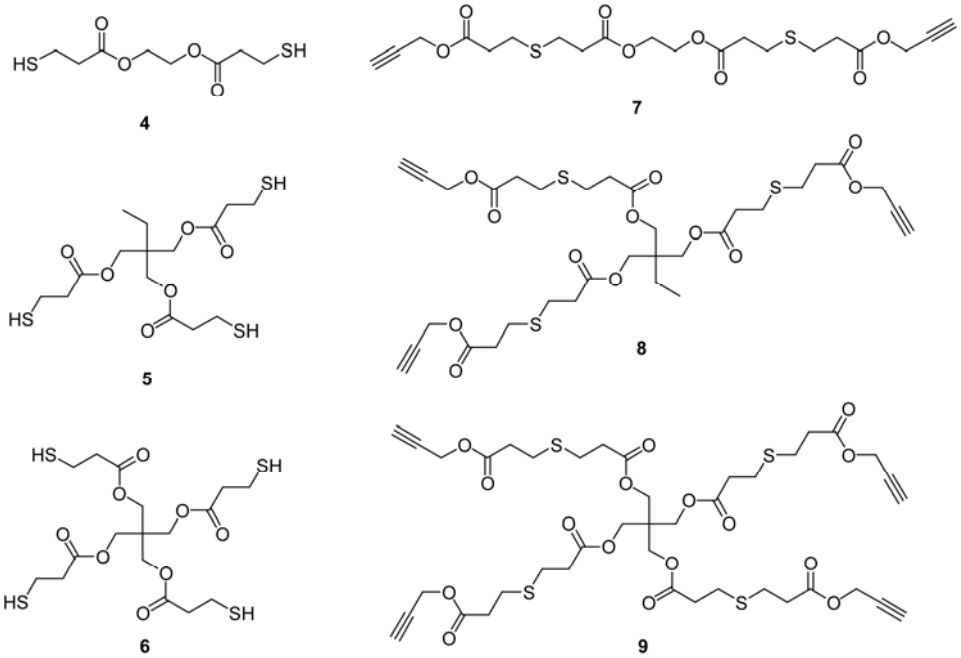

Figure 6 The thiol and alkyne monomers used for the preparation of polymer networks.

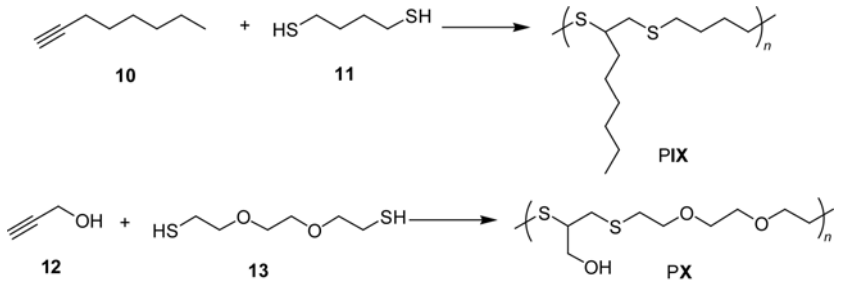

Figure 7 Preparation of linear main chain polymers by photo-initiated thiol-yne click polymerizations.

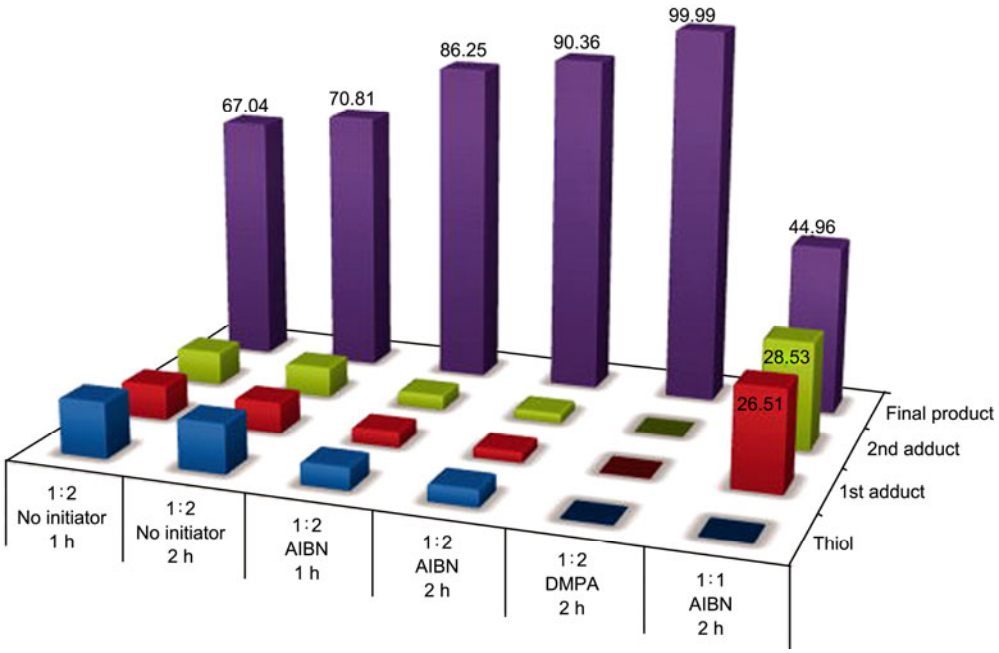

Figure 8 The comparison of reaction efficiency of thiol-yne additions initiated by DMPA, AIBN and non-catalyst respectively. Reproduced with permission from ref. [28]. Copyright 2012, Wiley-VCH.

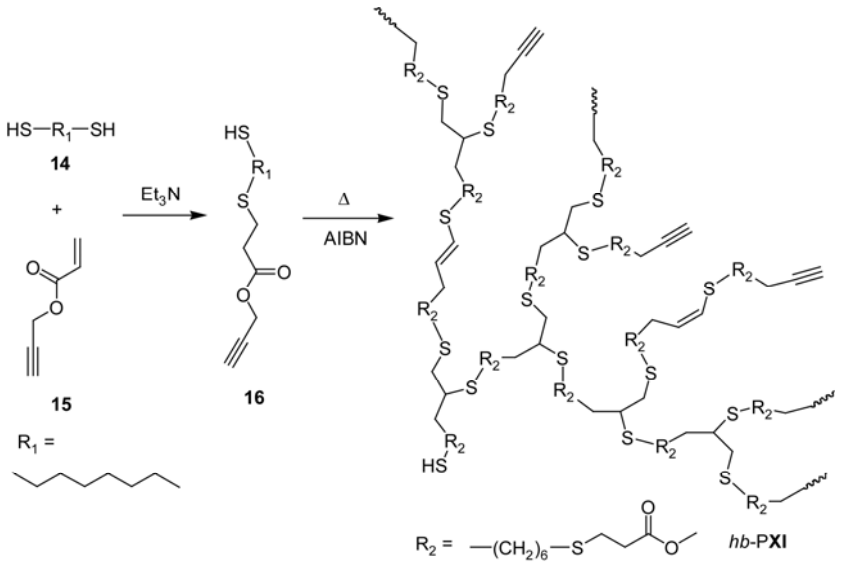

Figure 9 The sequential thiol-ene and thiol-yne click polymerization approach for the synthesis of *hb*-P**XI**.

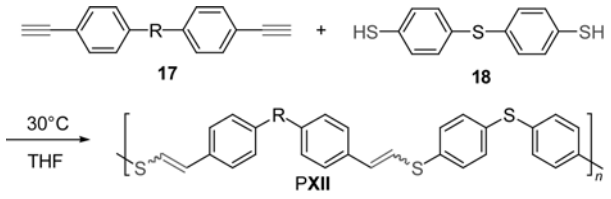

Figure 10 Synthesis of poly(vinylene sulfide)s via thermo-initiated thiol-yne click polymerizations of diynes **17** and dithiol **18**.

diynes, we could synthesize functional polymers. For example, the polymers with aggregation-enhanced emission characteristics could be prepared.

3 Amine-mediated thiol-yne click polymerization

During the course of exploring new polymerization reactions, we found the aroylacetylene or propiolate derivatives possess higher reactivity than the normal alkynes and could be polymerized with azide in the absence of metal catalyst. We thus successfully established the metal-free click polymerizations [35–39]. In 2010, we also established a novel amine-mediated thiol-yne click polymerization [17]. According to reported theory, propiolates are an inert alkyne when reacting with thiols via radical mediated mechanism [40]. Thus, our established polymerization must not share such mechanism.

As shown in Figure 11, the diphenylamine-mediated click polymerizations of dithiol **18** and dipropiolates **19**, carried out at room temperature for 24 h, readily furnished anti-Markovnikov products of PVSs with high molecular weights and high stereoregularities (*Z* content up to 81.4%) in high yields. Furthermore, the polymerization propagated smoothly without exclusion of air and moisture in the reaction systems, which will further simplify the polymerization procedures. The PVSs possess good film-forming ability, and are soluble, thermally stable, and optically transparent, making them promising candidates for photonic applications.

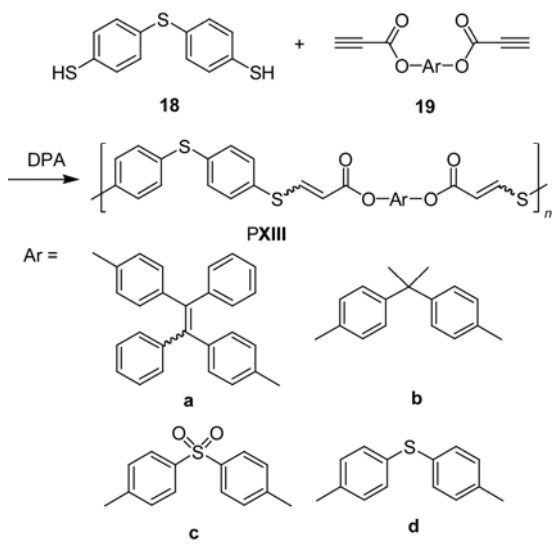

Figure 11 Synthesis of PVSs by thiol-yne click polymerizations of dithiol **18** and diynes **19**. DPA=diphenylamine.

4 Transition-metal-catalyzed thiol-yne click polymerization

The extensive studies on the thiol-yne reaction in the past half century have revealed that they proceed through Markovnikov and anti-Markovnikov addition routes to yield regio- and stereo-isomers with branched and linear structures (Figure 1) [41–43]. Besides the radical and amine-mediated reactions, the transition-metal complexes could catalyze the thiol-yne reaction and have been proven to be efficient catalysts for the preparation of regio- and stereo-regular vinyl sulfides. Several transition metal-based catalysts such as Rh, Ir, Ni, Pd, Pt, Au, and Zr have been developed [44–46]. Generally, the transition-metal-catalyzed thiol-yne reaction proceeds via a Migratory-Insertion mechanism [44].

Among the transition-metal complexes investigated, rhodium compounds have received considerable attention due to their high activity and their ability to catalyze the reaction to produce regio- and stereo-regular polymers under mild reaction conditions. Recently, our group developed the first example of Rh-catalyzed thiol-yne click polymerization for the synthesis of new electronically active sulfur containing acetylenic polymers P**XIV** (Figure 12) [18]. The $Rh(PPh_3)_3$-Cl-catalyzed click polymerizations of diynes **20** and dithiol **18** were carried out under mild conditions at room temperature, and PVSs of P**XIV** with high molecular weights (M_w up to 31500) in high yields were produced. Moreover, the polymerizations are functionality-tolerant and can proceed

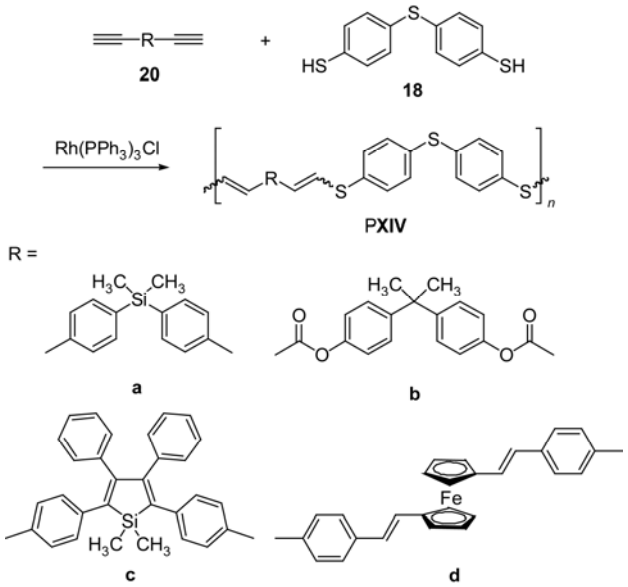

Figure 12 $RhCl(PPh_3)_3$-catalzyed thiol-yne click polymerizations to produce regio- and stereo-regular P**XIV**.

in regio- and stereo-selective manners (trans-isomer content up to unity). Interestingly, the stereo-structures of the polymers could be fine-tuned by engineering control on the sequential addition of monomers during the polymerization process and post-manipulation by light irradiation.

The synthesized polymers possess good solubility and film forming ability, and are optical transparent. All the polymer films exhibit higher refractive indices than conventional polymers due to the containing sulfur atoms. Furthermore, the functional pendants in diynes **20** have endowed P**XIV** with novel properties such as aggregation-enhanced emission, and ceramization capability to form semi-conducting nanoparticles. The polymers can also be readily cured by thermal treatment and UV irradiation, facilitating the fabrication of fluorescent photopatterns. All these features make P**XIV** promising optoelectronic candidates for real-world high-tech applications.

5 Conclusion and perspective

In this review, the recent progress of thiol-yne click polymerization was summarized. The photo-initiated thiol-yne click polymerization generally produces polymers with hyperbranched structures, whereas, the thermo-initiated, amine-mediated and transition-metal-catalyzed click polymerizations could yield linear polymers. Furthermore, the thiol-yne click polymerizations of aromatic alkynes and thiols will generate mono-additive polymers, which mechanism is needed to be further investigated. The synthesized polymers could be used as hydrogels, drug-delivery vehicles, cross-linked films, high refractive index optical materials, biomaterials etc.

Compared to the developed azide-alkyne and DA click polymerizations, the thiol-yne click polymerization possesses its advantages that the monomers are readily available without complicated synthetic procedures, its reaction conditions are simpler, and its produced polymers normally feature the high refractive indices due to the containing sulfur atoms. However, the synthesis of multifunctional aromatic thiols is not trivial task.

Although the researches in this area have being progressing rapidly, many possibilities are still waiting for exploration. Opportunities are plentiful but mainly exist in areas such as new monomer and topological structure design, catalyst development and application exploration. It is anticipated that through the collective research efforts, the thiol-yne click polymerizations will be further developed and find extensive applications in the synthesis of functional polymers and the development of advanced materials.

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